A Room Temperature Polyaniline/In_2O_3 Nanofiber Composite Based Layered ZnO/64° YX $LiNbO_3$ SAW Hydrogen Gas Sensor

A. Z. Sadek, W. Wlodarski, K. Kalantar-zadeh
Sensor Technology Laboratory, School of Electrical & Computer Engineering, RMIT University, Melbourne, Australia
Email: sadek@ieee.org

K. Shin[1] and R. B. Kaner[2]
[1]Department of Applied Chemistry, Sejong University, Seoul 143-747, KOREA
[2]Dept. of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, USA

Abstract—**A Polyaniline/In_2O_3 nanofiber composite based surface acoustic wave (SAW) gas sensor has been developed. Chemical oxidative polymerization of aniline was employed to synthesize polyaniline nanofibers with In_2O_3 nanoparticles. The nanocomposite was deposited onto a layered ZnO/64° YX $LiNbO_3$ SAW transducer. The sensor was exposed to various concentrations of H_2 gas and operated at room temperature. The sensor response was found to be 11 kHz towards 1% of H_2 in synthetic air. A fast response and recovery with good repeatability in a stable baseline condition were observed at room temperature.**

I. INTRODUCTION

Devices based on semiconductor metal oxide thin films have been extensively used for gas sensing based on film conductivity changes caused by interaction with gas molecules [1-3]. The gas sensing mechanism involves chemisorption of oxygen on the oxide surface followed by charge transfer during the reaction of chemisorbed oxygen with target gas molecules [4-5]. Intense research and development have been conducted to design highly sensitive, selective and stable gas sensors since Seiyama first observed gas sensing effects in metal oxides [6]. Recently, it has been reported [2-3], [7-9] that nanostructured forms of metal oxides has the potential to enhance the properties and performance of gas sensors because of the much higher surface to bulk ratio in nanomaterials compared to coarse micrograined materials.

Indium oxide is an n-type semiconductor, which has been widely used to detect H_2, NO_2, CO and O_3 gases [10-12]. However, such sensor requires an elevated temperature (100-350°C) for optimum operation which eventually reduces long term stability of the sensor. Also, an elevated temperature operation requires extra circuitry with high power consumption which reduces portability. Thus it would be highly desirable if the sensor could operate at room temperature with high sensitivity and fast response and recovery.

As an alternative to metal oxide materials, conducting polymers have received increasing interest for sensor design due to their room temperature operation, low production cost, ease of deposition onto a wide variety of substrates [13]. Among the family of conducting polymers, polyaniline is one of the most highly studied materials because of its simple synthesis, environmental stability and straightforward non-redox acid doping/base dedoping process to control conductivity [14-15].

Polyaniline gas sensors based on measuring resistance changes in thin film structures have been studied by a number of researchers [16-18]. A detailed review of polymer and polyaniline sensors can be found in references [19] and [20], respectively. However, traditional polyaniline is not as sensitive as metal oxides towards gas species. There have been several reports on improving polyaniline based sensor's sensitivity and selectivity using methods such as synthesis in the nanostructured forms [21-22], the addition of metal catalysts [23] and the combination of polyaniline and metal oxides [24-25]. Most literature reports on polyaniline nanostructures [21], [26-27] indicate that nanostructured polyaniline outperforms conventional polyaniline for gas sensing applications.

The combination of polyaniline and metal oxides in the nanostructured forms has the potential to increase sensitivity and selectivity at room temperature. The nanocomposite may retain the advantages of its constituents with increase surface functionalities for gas sensing. In addition, sensitivity, selectivity and long term stability of the sensors can be optimized by controlling the volume ratio of polyaniline nanofibers to metal oxide nanoparticles. In this paper, a polyaniline/In_2O_3 nanocomposite sensitive layer was formed on the layered SAW transducer. Finally, the responses of the sensor to different H_2 gas concentrations were investigated.

II. EXPERIMENTAL

In this work, a layered SAW device is used as the transducing platform. The substrate is 64° YX $LiNbO_3$ with an intermediate ZnO protective layer. Shear-horizontal (SH) leaky surface acoustic wave is the dominant mode in this layered substrate. The sensor consisted of two-port resonators with 38 electrode pairs in the input and output Inter Digital Transducers (IDT), 160 electrodes in each

1-4244-0376-6/06/$20.00 ©2006 IEEE

Authorized licensed use limited to: RMIT University. Downloaded on November 19, 2008 at 22:48 from IEEE Xplore. Restrictions apply.

reflective grating, 700 µm aperture width and a periodicity of 40 µm. The center-to-center distance between the IDTs was 1920 µm. The IDTs were formed by patterning an 80 nm layer of gold and a 20 nm titanium layer. The titanium layer is added to improve adhesion of the gold film.

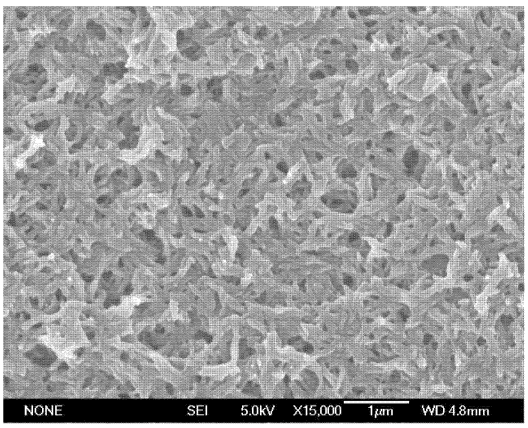

Figure 1. SEM image of a polyaniline/In_2O_3 nanofiber composite.

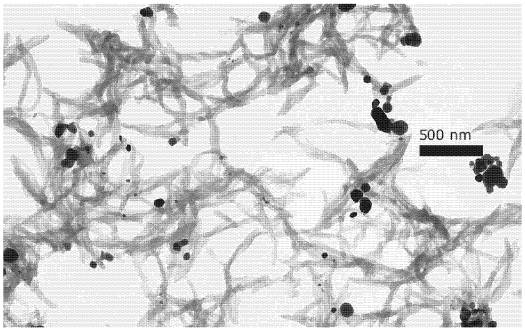

Figure 2. TEM image of a polyaniline/In_2O_3 nanofiber composite [28].

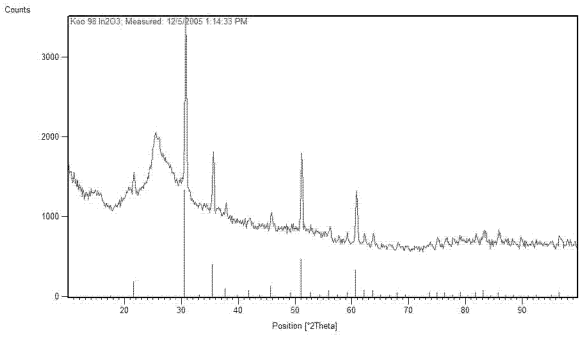

Figure 3. XRD pattern of a polyaniline/In_2O_3 nanofiber composite [28].

A ZnO layer of 1.2 µm in thickness was deposited on the surface of the 64° YX $LiNbO_3$ substrates to form the layered structure. A radio frequency (RF) magnetron sputterer was used to deposit from a 99.99% pure ZnO target with rf power of 120 W. The sputtering gas was 40% O_2 in Ar with a pressure of 10^{-2} torr, the substrate temperature was 260°C and the deposition time was for periods of 60 minutes.

In this paper the chemical polymerization technique has been employed to fabricate PANI/In_2O_3 nanocomposite on the surface of a layered ZnO/64° YX $LiNbO_3$ substrate. At first, aniline monomer was added into the 1.0 M camphor sulfonic acid (CSA) solution of In_2O_3 nanoparticles. The concentration of aniline monomer to In_2O_3 is 5 to 1 on the solution. Then ammonium persulfate was added to the mixture and allowed to react for overnight. The product was washed with 1.0 M NaOH solution and further purified by four cycles of washing with distilled water centrifugation. The nanocomposite solution was drop cast onto the active area of the transducers using a micropipette. They were then left to dry in a clean, dry environment for one day. The gas sensor is made up of two important physical components: the sensitive polyaniline/In_2O_3 nanofiber composite layer, which interacts with the gas media by changing conductivity, and the SAW transducer, which changes its operating frequency with any conductivity change. Using the layered SAW device as a positive feedback element in a closed loop circuit with an amplifier, an oscillator was formed. A frequency counter was used to measure the operational frequency of the transducer upon exposure to the H_2 gas. The operational frequency of the sensor was found to be approximately 107.2 MHz in dry synthetic air at room temperature.

The sensor was mounted inside an enclosed environmental cell. The four mass flow controllers (MFCs) were connected to form a single output that supplied gas to the cell. A constant flow rate of 0.2 liters per minute was delivered via the MFCs. A computerized gas calibration system was used to vary the concentration of H_2 gas in synthetic air and to measure the operating frequency of the sensors. The sensor responses were displayed in real-time and saved for off-line processing and analysis. Gas exposure time was fixed for each pulse of H_2 gas and the cell was purged with synthetic air between each pulse to allow the surface of the sensor to recover to atmospheric conditions. The sensor was exposed to a hydrogen gas pulse sequence of 0.06%, 0.12%, 0.25%, 0.50%, 1%, and 0.12% concentrations in synthetic air at room temperature. A Fluke high-resolution counter (PM66860B) was used to measure the operational frequency.

III. Results

Structural Characterization: The average thickness of the PANI/In_2O_3 nanofiber layer on the substrate was measured by profilemeter is 0.4 µm. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the nanocomposite are shown in Figs. 1 and 2, respectively. The average diameters of the nanofibers are 90 nm and they are connected together in a network. From TEM image it was found that In_2O_3 nanoparticles are embedded into the polyaniline nanofibers backbone. From SEM and TEM images, it can be concluded that the deposited thin film is porous. An x-ray diffraction (XRD) pattern is shown in Fig. 3, in which the sharp line-peaks in the bottom are due to the pure In_2O_3 from JCPDS database and the peaks in the above are due to the PANI/In_2O_3 nanocomposite samples. The diffraction peaks from the

Authorized licensed use limited to: RMIT University. Downloaded on November 19, 2008 at 22:48 from IEEE Xplore. Restrictions apply.

nanocomposite sample are well match with the sharp lines from the pure In_2O_3 which indicate the sample contains In_2O_3 particles.

Electrical Characterization: Dynamic response to a sequence of different H_2 gas concentrations in synthetic air is shown in Fig. 4. In a SAW device, the change in electrical conductivity of the sensing layer perturbs the velocity of the propagating acoustic wave due to the piezoelectric effect. The center frequency of a SAW device is given by the equation, $v = fp$, where v is the surface wave velocity, f is the center frequency and p is the interdigitated transducer period. The introduction of H_2 gas to the sensor surface causes reduction of the device's resonant frequency. With hydrogen exposure, the conductivity of the polyaniline/In_2O_3 nanofiber composite layer increases resulting in a decrease in the acoustic wave velocity, thereby decreasing the resonant frequency. This change in frequency is related to the concentration of H_2 present in the environment.

The sensor response is defined as the variation in operating frequency of oscillation due to the interaction with target gas. Measured sensor response was approximately 11 kHz towards 1% of H_2 in synthetic air. The 90% response time of 30 s and recovery time of 40 s with good repeatability were observed at room temperature. The response magnitude variation for the sensor to different H_2 concentrations at room temperature is shown in Fig. 5. The frequency shift increases non-linearly with the increase of H_2 concentrations and saturating for large concentrations.

The mechanism of hydrogen interactions with In_2O_3 is well known. Hydrogen is a reducing agent for the n-type In_2O_3 nanoparticles, increasing its conductivity on interaction. During the interaction process, the analyte dissociates onto the surface of the In_2O_3 by injecting electrons. These free electrons reduce the surface depletion region, thereby increase the surface conductivity. However, the mechanism for polyaniline and H_2 interactions is still unclear. Our previous experimental results [29] show that conductivity of polyaniline increases on exposure to H_2. The hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some of the imine nitrogens [30]. It has also been suggested that the resistance change is caused by the formation of water [24].

The mechanism for the conductivity change in the polyaniline/In_2O_3 nanofiber composite layer due to the interaction with the H_2 is not yet understood. However, we propose two possible mechanisms for H_2 sensing. The first one is activation of the hydrogen by In_2O_3 due to formation of indium-dihydrogen complexes. The second one is an interaction with the polyaniline backbone possibly facilitated by In_2O_3 which may induce dissociation of the hydrogen leading to either a doping type response or chain alignment.

Reproducibility was observed as indicated when a second pulse of 0.12% of H_2 was introduced into the sensor chamber. It was found that the polyaniline/In_2O_3 nanofiber composite based sensor produce repeatable responses of the same magnitude with good baseline stability. Repeatability was confirmed by testing the sensor continuously over a 5 day period.

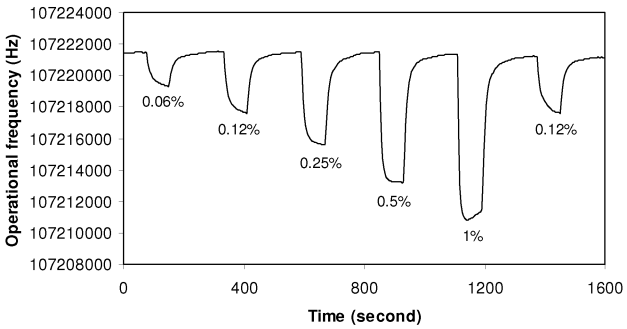

Figure 4. Dynamic response of a polyaniline/In_2O_3 nanofiber based ZnO/64° YX $LiNbO_3$ SAW sensor towards different concentrations of H_2 at room temperature [28].

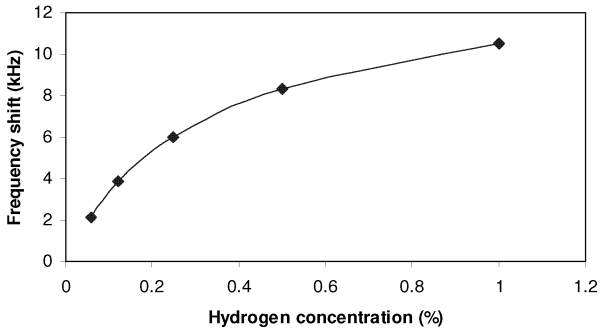

Figure 5. Frequency shift (kHz) versus H_2 gas concentrations (%) at room temperature.

IV. CONCLUSIONS

We have fabricated SAW gas sensor based on PANI/In_2O_3 nanofiber composite synthesized by chemical oxidative polymerization. The sensor has been investigated towards H_2 gas. The sensor showed a repeatable and large response towards H_2 gas. A fast response and recovery time with stable base-line frequency was observed at room temperature. Due to room temperature operation, the gas sensor is promising for environmental and industrial applications.

ACKNOWLEDGMENT

The UCLA group would like to thank the Microelectronics Advanced Research Corp. Center on Functional Engineered NanoArchitectonics (MARCO-FENA) for financial support.

REFERENCES

[1] D. Kohl, "Surface processes in the detection of reducing gases with SnO_2-based devices," Sens. Actuators B: Chem. vol. 18, pp. 71-113, 1989.

Authorized licensed use limited to: RMIT University. Downloaded on November 19, 2008 at 22:48 from IEEE Xplore. Restrictions apply.

[2] E. Comini, G. Faglia, G. Sberveglieri, Z. Pan, and Z. L. Wang, "Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts," Appl. Phys. Lett. vol. 81, pp. 1869–1871, 2002.

[3] A. A. Tomchenko, G. P. Harmer, B. T. Marquis, "Detection of chemical warfare agents using nanostructured metal oxide sensors," Sens. Actuators B: Chem., vol. 108, pp. 41-55, 2005.

[4] P. Esser and W. Gopel, "Physical adsorption on single crystal zinc oxide," Surf. Sci., vol. 97, pp. 309-318, 1980.

[5] S. R. Morrison, Chemical sensors in semiconductor sensors, John Wiley, New York, 1994.

[6] T. Seiyama, A. Kato, K. Fujiishi, and M. Nagatani, "A new detector for gaseous components using semiconductive thin films," Anal. Chem., vol. 34, pp. 1502-1503, 1962.

[7] R. Ionescu, A. Hoel, C. G. Granqvist, E. Llobet, and P. Heszler, "Low-level detection of ethanol and H_2S with temperature-modulated WO_3 nanoparticle gas sensors," Sens. Actuators B: Chem., vol. 104, pp. 132-139, 2005.

[8] J. L. Solis, S. Saukko, L. B. Kish, C. G. Granqvist, and V. Lantto, "Nanocrystalline tungsten oxide thick films with high sensitivity to H_2S at room temperature," Sens. Actuators B: Chem., vol. 77, pp. 316–321, 2001.

[9] N. Yamazoe, "New approaches for improving semiconductor gas sensors," Sens. Actuators B: Chem., vol. 5, pp. 7–19, 1991.

[10] G. Korotcenkov, V Brinzari, A Cerneavschi, M Ivanov, A Cornet, J Morante, A Cabot and J Arbiol, "In_2O_3 films deposited by spray pyrolysis: gas response to reducing (CO, H_2) gases," Sensors and Actuators B, vol. 98, pp. 122-129, 2004.

[11] M. Ivanovskaya, A. Gurlo and P. Bogdanov, "Mechanism of O_3 and NO_2 detection and selectivity of In_2O_3 sensors," Sensors and Actuators B, vol. 77, pp. 264-267, 2001.

[12] A. Gurlo, N. Bârsan, M. Ivanovskaya, U. Weimar and W. Göpel, "In_2O_3 and MoO_3–In_2O_3 thin film semiconductor sensors: interaction with NO_2 and O_3," Sensors and Actuators B: Chemical, vol. 47, pp. 92-99, April 1998.

[13] J. Janata and M. Josowicz, "Conducting polymers in electronic chemical sensors," Nat. Mater., vol. 2, pp. 19-24, 2003.

[14] W. S. Huang, B. D. Humphrey, and A. G. MacDiarmid, "Polyaniline a novel conducting polymer: Morphology and chemistry of its oxidation and reduction in aqueous electrolytes," J. Chem. Soc. Faraday Trans., vol. 82, pp. 2385-2400, 1986.

[15] P. Chandrasekhar, Conducting polymers fundamentals and applications: A practical approach, Boston, Kluwer Academic Publishers, 1999.

[16] S. Roy, S. Sana, B. Adhikari, and S. Basu, "Preparation of doped polyaniline and polypyrrole films and applications for hydrogen gas sensors," J. Polym. Mater., vol. 20, pp. 173-180, 2003.

[17] N. E. Agbor, M. C. Petty, and A. P. Monkman, "Polyaniline thin films for gas sensing," Sens. Actuators B: Chem., vol. 28, pp. 173-179, 1995.

[18] D. Xie, Y. W. Pan, D. Li, Z. Wu, and Y. Li, "Fabrication and characterization of polyaniline-based gas sensor by ultra-thin film technology," Sens. Actuators B: Chem., vol. 81, pp. 158-164, 2002.

[19] B. Adhikari and S. Majumdar, "Polymers in sensor applications," Prog. Polym. Sci., vol. 29, pp. 699-766, 2004.

[20] D. N. Debarnot, F. P. Epaillard, "Polyaniline as a new sensitive layer for gas sensors," Analytica Chimica Acta., vol. 475, pp. 1-15, 2003.

[21] J. Huang, S. Viriji, B. H. Weiller and R. B. Kaner, "Nanostructured polyaniline sensors," Chem. Eur. J., vol. 10, pp. 1314-1319, 2004.

[22] J. Huang and R. B. Kaner, "The intrinsic nanofibrillar morphology of polyaniline," Chem. Comm., vol. 4, pp. 367-376, 2006.

[23] A. A. Athawale, S. V. Bhagwat and P. P. Katre, "Nanocomposite of Pd-polyaniline as a selective methanol sensor," Sens. Actuators B: Chem., vol. 114, pp. 263-267, 2006.

[24] C. Conn, S. Sestak, A. T. Baker and J. Unsworth, "A polyaniline-based selective hydrogen sensor," Electroanal., vol. 10, pp. 1137-1141, 1998.

[25] N. Parvatikar, S. Jain, S. Khasim, M. Revansiddappa, S. V. Bhoraskar and M. A. Prasad, "Electrical and humidity sensing properties of polyaniline/WO_3 composites," Sens. Actuators B: Chem., vol. 114, pp. 599-603, 2006.

[26] S. Virji, J. Huang, R. B. Kaner, and B. H. Weiller, "Polyaniline nanofiber gas sensors: Examination of response mechanisms," Nanoletters., vol. 4, pp. 491-496, 2004.

[27] D. Aussawasathien, J. -H. Dong, and L. Dai, "Electrospun polymer nanofiber sensors," Synth. Met., vol. 154, pp. 37-40, 2005.

[28] A. Z. Sadek, W. Wlodarski, K. Shin, R. B. Kaner, and K. Kalantar-zadeh, "A layered surface acoustic wave gas sensor based on a polyaniline/In_2O_3 nanofibre composite," Nanotechnology, vol. 17, pp. 4488-4492, 2006.

[29] A. Z. Sadek, C. O. Baker, D. A. Powell, W. Wlodarski, R. B. Kaner, and K. Kalantar-zadeh, "Polyaniline nanofiber based surface acoustic wave gas sensors – Effect of nanofiber diameter on H_2 response," IEEE Sensors J., in press.

[30] A. G. MacDiarmid, Presentation at DOE Center of Excellence on Carbon-based H_2 storage, USA, May 24, 2005. [Online]. Available: http://www.hydrogen.energy.gov/pdfs/review05/stp_42_macdiarmid.pdf

Authorized licensed use limited to: RMIT University. Downloaded on November 19, 2008 at 22:48 from IEEE Xplore. Restrictions apply.